Seasonal Changes in As, Bi, Cd, Mo and halogen elements recorded in Greenland EastGRIP snow pit

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On July 2017, a series of 38 snow samples were collected from 1.9 m deep snow pit at the Greenland EastGRIP deep ice core drilling camp in 5 cm interval. We determined As, Ba, Bi, Cd, Mo and halogen elements together with water stable isotope ratios ($\delta^{18}O$) and ion species such as Na^+, Ca^{2+}, MSA (methylsulfonic acid), and SO_4^{2-} from these samples.

Well defined $\delta^{18}O$ record indicates that the 1.9m deep snow pit samples cover 4.5 years from 2012 winter to 2017 summer. The concentration records of Ca^{2+} Na^+, SO_4^{2-} and Ba generally show peaks during spring seasons. This implies the large increases of atmospheric input of crust dust and sea salt for that season as well as other Greenland snow and icecore records. However, nss-SO_4^{2-} also showed large peak from 2014 fall to 2015 spring. This is most likely due to the eruption of Holuhraun volcanoe, Iceland.

As, Bi, Cd and Mo are known to be largely contributed by volcanic eruption. However, in our samples, no significant enrichment of these elements were found for the period of 2014~2015. Only Cd showed 2~3 times increase of crust enrichment factor (EFc). Considering the high EFc values of As, Bi, Cd and Mo over all samples, these elements seem to be significantly enriched by anthropogenic emissions, and thus the volcanic contributions were relatively small. In additions, Holuhraun eruption was known to be gas rich and ash poor. This also well supports the little influence of that volcanic eruption on the atmospheric input of the trace metals. Halogen elements such as Br and I reveal the seasonal change of these elements are characterized by summer peak. This represents that the atmospheric input of Br and I are related to bio-activities in polar region which is maximized during summer season.

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PURPOSE OF THIS RESEARCH

- Characterization of seasonal changes in atmospheric aerosols input into the Northeastern Greenland
- Identification of sources for atmospheric aerosols over the Northeastern Greenland
- Evaluation for natural/anthropogenic contributions to the atmospheric trace elements.

SAMPLING

- In July, 2017, a series of 38 snow samples collected from 1.9 m deep snow pit at the Greenland EGRIP camp (75.623°N, 35.96°W).
- The snow pit was hand-dug by the researcher wearing full clean room garments and PE gloves using plastic shovel.
- The snow samples were collected at every 5 cm from the up-wind wall of the snow pit by pushing an acid clean cylindrical Teflon containers.

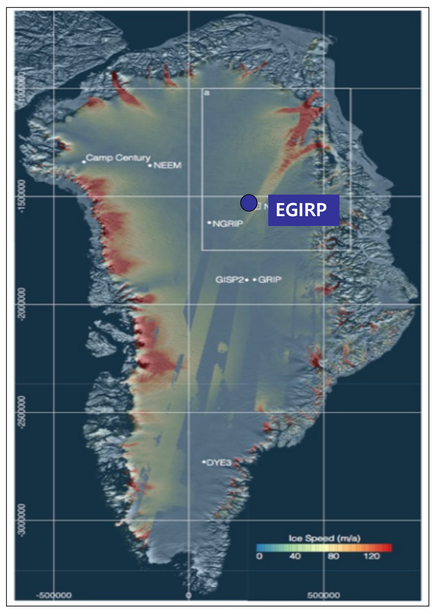

Figure 1. Map of Sampling site

Figure 2. EGRIP snow pit Sampling

ANALYSIS

- All sample preparation and measurements except water stable isotopes measurement were performed in a Class 10 clean booth in a Class 1000 clean laboratory.
- Water stable isotope ratios ($\delta^{18}O$ and δD) of snow samples were measured by CRDS (2130-i, PICARRO Inc.).
- Ion species – Na^+, Ca^{2+}, SO_4^{2-} and MSA in snow samples were determined using ion chromatography (ICS 2100, Dionex) with CS12A(4 x 250 mm) and AS15(2x250 mm) columns.
- Trace metals and halogen in snow samples were analyzed using ICP-SF-MS (Element2, Thermo Fisher SCIENTIFIC, Germany) equipped with APEX_HF(Desolvation System, ESI, USA).

Figure 3. (a) Class 10 Clean booth (b) CRDS (c) Ion Chromatography (d) ICP-SF-MS and APEX_HF

RESULTS AND DISCUSSION

1. Age dating

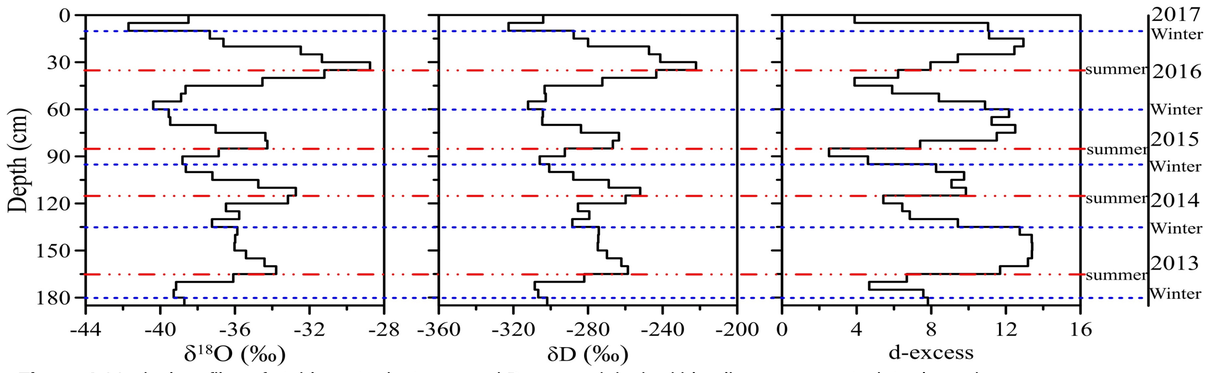

Figure 4. Vertical profiles of stable water isotopes and D-excess (dashed blue lines represent winter layers)

- The age dating of snow samples was primarily determined by annual cycles of water stable isotope ratios ($\delta^{18}O$ and δD).
- The less negative values of $\delta^{18}O$ and δD at 35, 85, 115, 165cm were assigned to summer season, while the more negative values at 10, 60, 95 and 135cm to winter season.
- According to the records of $\delta^{18}O$ and δD, 1.9m deep snow pit covers four and half years from 2013 to 2017 summer.
- The mean accumulation rate of 132mm w.e. well met the other Greenland snow/ice cores.

2. Seasonal variations and Holuhraun eruption

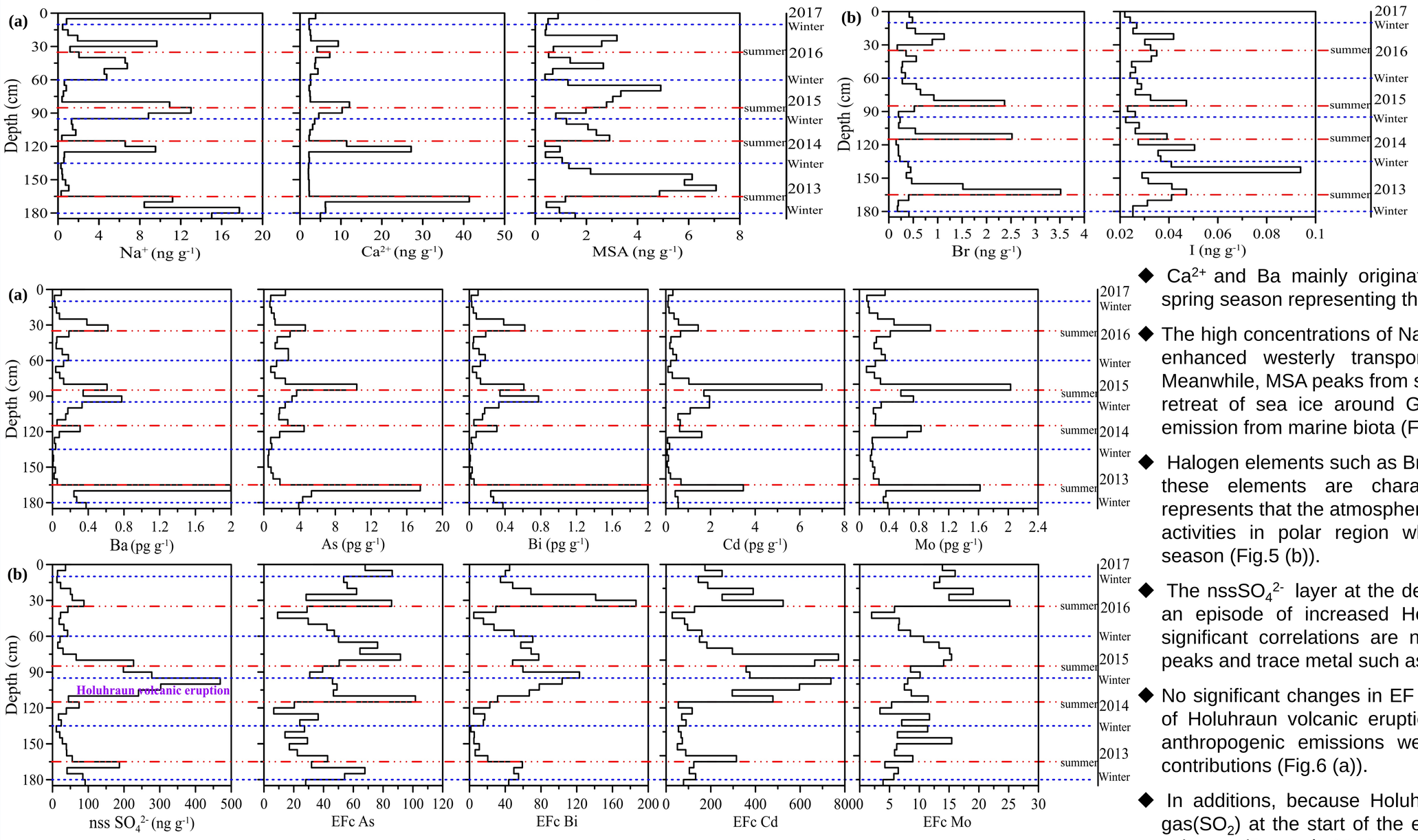

Figure 5. (a) Vertical profiles of ion concentrations (Na^+, Ca^{2+} and MSA) (b) Vertical profiles of Halogen concentrations

Figure 6. (a) Changes in concentrations (in pg g^{-1}) in the snow from the surface to 1.85m. (b) Crustal enrichment (relative to Ba) factors (EFc) for snow pit samples

- Ca^{2+} and Ba mainly originating from crust dust peaked during spring season representing the large influence from Asian dust.
- The high concentrations of Na^+ during the spring season imply that enhanced westerly transport more sea-salt for that period. Meanwhile, MSA peaks from summer to autumn seem to be due to retreat of sea ice around Greenland and thus increased DMS emission from marine biota (Fig.5 (a)).
- Halogen elements such as Br and I reveal the seasonal change of these elements are characterized by summer peak. This represents that the atmospheric input of Br and I are related to bio-activities in polar region which is maximized during summer season (Fig.5 (b)).
- The $nssSO_4^{2-}$ layer at the depth of 85-120 cm is associated with an episode of increased Holuhraun eruption inputs. However, significant correlations are not observed between the $nssSO_4^{2-}$ peaks and trace metal such as As, Bi, Cd and Mo (Fig.6 (b)).
- No significant changes in EF of As, Bi, Cd, and Mo for the period of Holuhraun volcanic eruption represent the contributions from anthropogenic emissions were much larger than the volcanic contributions (Fig.6 (a)).
- In additions, because Holuhraun eruption released much more gas(SO_2) at the start of the event, the eruption was gas rich and ash poor (Du et al., 2019, *Envrion. Earth, Sci.*).

ACKNOWLEDGEMENT

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